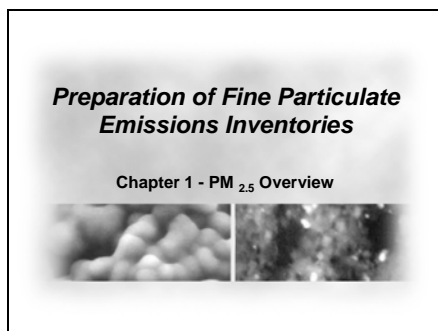


Chapter 1 - PM 2.5 Overview

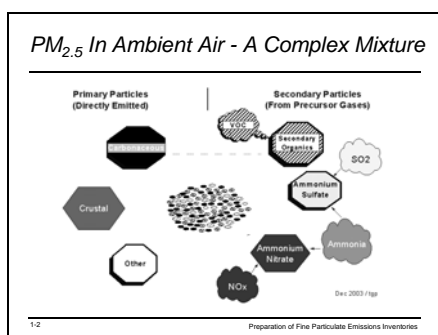
1 - 1



After this lesson, participants will be able to describe:

- the general composition of fine particulate matter in the atmosphere,
- how fine particulate matter are formed, and
- sources that contribute to the formation of fine particulate matter.

1 - 2



This graphic illustrates the difference between **primary**, or directly emitted particles and **secondary** particles, which are formed in the atmosphere from precursor gases.

Primary particles contain:

- elemental carbon (EC)
- primary organic aerosol (POA)
- small amounts of crustal matter and other materials.

Secondary particles contain:

- secondary organic aerosol (SOA) formed from volatile organic compounds
- ammonium sulfate formed from SO₂ and ammonia gases
- ammonium nitrate, formed from NO_x and ammonia gases.

The term **total carbonaceous matter** is used to describe the combined mass of EC, POA, and SOA.

1 - 3

Urban PM Sites

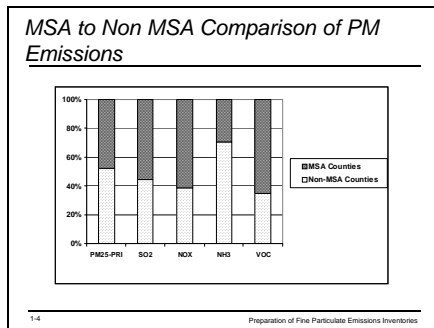
- Eastern U.S. data is very homogenous
- Comprised mostly of carbon
- Ammonium and sulfate components combined are comparable to carbon
- Crustal component is very small

1-3 Preparation of Fine Particulate Emissions Inventories

Data from EPA's urban speciation trends network show that:

- particulate matter in the eastern half of the United States is homogenous in composition
- particulate matter in eastern sites comprises mainly carbonaceous aerosol and ammonium sulfate in comparable amounts
- the crustal component of PM_{2.5} is very small in both western and eastern urban monitoring sites (with the exception of some places in the southwest and the central valley of California)

1 - 4



This graph depicts percentages of primary PM emissions (and their precursors) throughout the 37 states of eastern and central United States.

The data indicate that:

- roughly half of the primary PM is emitted in the Metropolitan Statistical Areas and about half in the rural areas.
- ammonia (NH₃) is the only precursor with greater emissions in rural areas than in urban areas;

Higher rural ammonia emissions are related to agricultural emissions. In urban areas, these emission can be attributed to agricultural and mobile sources.

1 - 5

Comparison of Urban and Rural Data

- More sulfate than carbon in non-urban sites
- Sulfate concentration slightly higher in urban areas
- Carbon concentrations substantially higher in urban areas
- Conclusions
 - Sulfate is a regional problem
 - Carbon has a regional component with urban excess
- Urban Excess definition

1-5

Preparation of Fine Particulate Emissions Inventories

Ambient monitoring data from both urban and rural sites in the speciation trends network show:

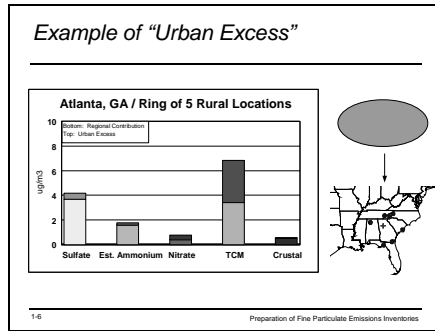
- higher quantities of sulfate than carbon in the non-urban sites
- slightly higher sulfate concentrations in urban areas compared with surrounding non-urban areas
- substantially higher carbon concentrations in urban areas

Conclusions to be drawn:

- The monitoring data highlights the regional scope of the problem of sulfate emissions.
- There is a significant excess of carbon in the urban areas, as evidenced by its marked increase from rural to urban areas.

Urban air quality data is often compared to rural air quality data by noting the amount of "urban excess" for a particular component.

1 - 6

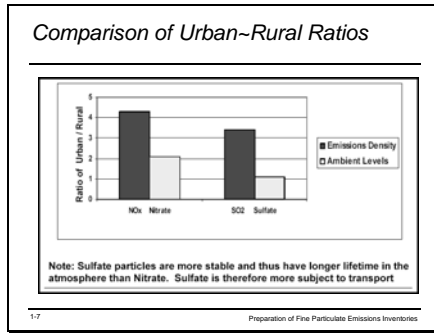


- Data from Atlanta, GA is presented in this graph to illustrate the "urban excess" concept, as depicted on the top part of the bars.

Note that:

- Nearly all sulfate is associated with the regional contribution; this indicates that the sulfate in Atlanta is only 10-15% higher in concentration than the sulfate that you find in the surrounding rural sites.
- Since most of the ammonium is associated with sulfate, ammonium concentrations follow a similar pattern.
- Nitrate and carbon concentrations are nearly twice as high in urban areas as in rural areas, a significant "excess".
- The concentration of total carbonaceous material is greater than the sulfate concentrations in Atlanta and the concentration of crustal material is very small.

1 - 7



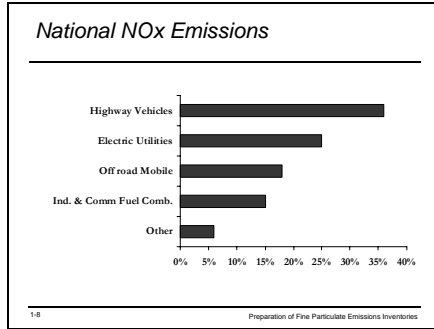
This bar chart compares emission densities with ambient concentrations for urban and rural areas.

- The density of NO_x emissions per square mile is about four times higher in urban areas than in rural areas
- Nitrate concentrations are roughly twice as high in urban areas as in the rural areas.
- The data suggest that the higher concentration of ammonium nitrate in urban areas is associated with the higher NO_x emissions in the urban areas.
- Sulfate has a higher density of emissions in urban areas, but this ratio is not reflected in the ambient data.
- The lack of an urban excess of sulfate in Atlanta is typical throughout the eastern United States.

Reasons for the difference between urban excesses for nitrates and sulfates:

- the NO_x to nitrate reaction occurs fairly quickly, before it can be transported very far
- nitrate is less stable and may revert to other compounds during transport
- sulfate has a very long lifetime; once converted from SO₂, sulfate particles can last for weeks and be transported long distances.
- Although the emission density of SO₂ is much higher in urban areas than in rural areas, the concentrations are fairly uniform over broad geographic areas.
- Consequently, sulfate is considered a regional pollutant in terms of the impact on PM_{2.5}.

1 - 8



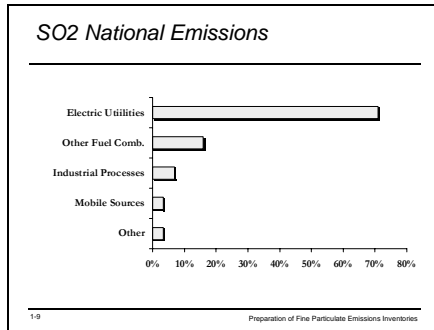
National data indicate that NO_x emissions are about 23 million tons a year.

This graph identifies NO emission sources as follows:

- 35% are from highway vehicles
- 25% are from electric utilities
- 18% are from mobile sources, and
- 15% are from industrial and commercial fuel combustion.

All of these NO_x emission sources are associated with fuel combustion. The “Other” category represents emissions from industrial processes.

1 - 9

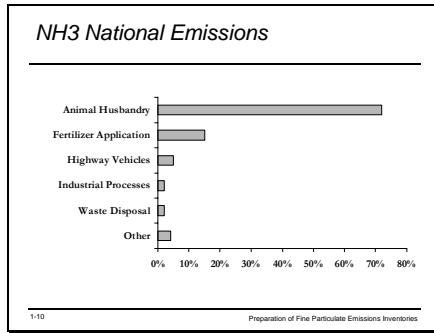


This graph identifies electric utilities as the source of 70-75% of national SO₂ emissions.

Although electric utility emissions tend to be more highly concentrated in urban areas, sulfate emissions impact large geographical areas.

This impact is due to the long lifetime of sulfate particles and their transportability over long distances.

1 - 10



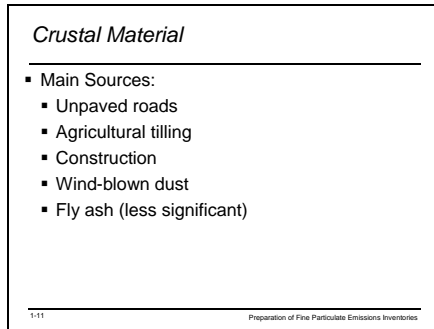
This graph identifies sources of national ammonia emissions as follows:

- Animal husbandry, specifically associated with cattle, hogs, and poultry, represents a significant source of ammonia emissions.
- Smaller amounts of ammonia emissions are associated with animal waste and waste processing procedures.
- Fertilizer application is a source of approximately 15-20% of the ammonia.
- Highway vehicles represent a small percentage of the emissions, which can be important in an urban area.

Ammonia emissions are dispersed across large portions of the east and the Midwest, regions with a higher concentration of farms where animals are raised.

This is consistent with the pattern of measured ammonium ion deposits from the National Atmospheric Deposition Program.

1 - 11



Crustal material mainly comes from fugitive dust.

The main sources of fugitive dust are unpaved roads, agricultural tilling, construction, and wind-blown dust, which primarily occurs in the arid areas of the western United States.

A less significant source of crustal material is fly ash from coal- or oil-fired boilers, which is chemically similar to crustal material.

1 - 12

Crustal Material (cont.)

- Huge Disparity Between EI & Ambient Data
 - Ambient Data
 - < 1 ug/m³ in most of US
 - Exception: > 1 ug/m³ in much of Southwest
 - Emissions: 2.5M TPY (comparable to Carbon Emissions)

1-12 Preparation of Fine Particulate Emissions Inventories

A disparity exists between the crustal data in an emissions inventory and the crustal material found in ambient air quality samples.

Ambient data indicate that less than one microgram per cubic meter of crustal material exists in the U.S., with the exception of the southwest.

Emissions inventory data indicate that PM_{2.5} emissions are about 2.5 million tons a year, which is comparable to the carbon emissions.

1 - 13

Crustal Material (cont.)

- Fugitive Dust has low "Transportable Fraction"
- Crustal materials are a relatively small part of PM_{2.5} in the ambient air
- Fugitive dust is released near the ground and surface features often capture the dust near its source
- As much as 50-90% may be captured locally

1-13 Preparation of Fine Particulate Emissions Inventories

Fugitive dust emissions:

- are emitted very close to the ground and get trapped in shrubbery, vegetation, buildings, etc.
- may not be transported far from where they are released
- air quality dispersion models fail to recognize that much fugitive dust will be deposited within a few hundred yards to a few miles of the source

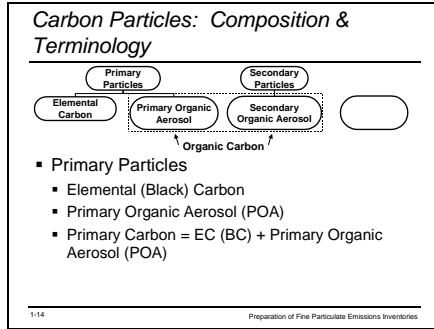
Estimates indicate that about half of the fugitive dust emitted in eastern metropolitan areas is removed by surface features near the source.

This inventory adjustment only applies to regional chemical transport modeling. Thus, this adjustment is made in the emissions processor, not in the emissions inventory.

In summary:

- crustal materials are a relatively small part of PM_{2.5} in the ambient air
- fugitive dust is released near the ground, and surface features often capture the dust near its source

1 - 14



Carbon is a major component of PM_{2.5} in the ambient air.

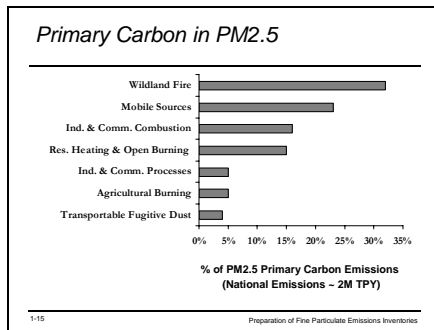
You may recall that carbon particles can be either primary (or directly emitted), or secondary organic aerosol particles that are formed in the atmosphere primarily from volatile organic compounds.

Primary carbon particles are made of:

- elemental or black carbon,
- primary organic aerosols.

Approximately 20% of the primary carbon emissions are EC and the other 80% are POA.

1 - 15



Data show that sources of primary carbon emissions nationwide are:

- wildfires
- mobile sources
- industrial and commercial combustion
- residential heating and open burning
- burning of construction debris
- industrial and commercial processes, agricultural burning
- fugitive dust

Nationally, crustal material is emitted at about 2.5 million tons per year, as compared to about 2 million tons per year of primary carbon emissions.

However, carbon emissions are more abundant in the ambient air.

1 - 16

<i>POA & EC Characteristics of Primary Carbon Emissions</i>		
Category	Ratio of organic carbon mass* to elemental carbon mass (average)	Potential range of ratios
Forest Fires	9.9	6 - 28
Managed Burning	12	6 - 28
Agricultural Burning	12	2.5 - 12
Open Burning - Debris	9.9	
Non-road Diesel Engines & Vehicles	0.4	0.4 - 3
On-road Diesel Vehicles	0.4	0.4 - 3
Trains, Ships, Planes	0.4	0.4 - 25
Non-road Gas Engines & Vehicles	14	0.25 - 14
On-road Gas Vehicles	4.2	0.25 - 14
Fugitive Dust - Roads	22	3 - 65
Woodstoves	7.4	3 - 50
Fireplaces	7.4	3 - 50
Residential Heating - Other	26	
Commercial Cooking	111	13 - 111

The ratio of POA mass to EC mass for most sources is roughly 10 to 1.

Elemental carbon represents a higher ratio than organic carbon in diesel engines, diesel-powered vehicles, ships, trains, and planes.

The higher elemental to organic carbon ratio in diesels is due partially to the higher combustion temperatures in diesel-fueled engines, which tend to combust the organic carbon more completely.

Conversely, the lower temperature combustion processes will emit more organic matter, as a result of less complete combustion.

1 - 17

<i>Primary Organic Aerosols (POA)</i>
<ul style="list-style-type: none"> ▪ Certain organic carbon excluded ▪ Organic carbon matter = primary organic aerosol (POA). ▪ The OC to POA multiplier for "fresh" POA in the emissions is usually estimated ▪ Particles "age" through oxidation. ▪ A different "multiplier" is applied to the POA by the chemical transport models to account for the "aging"

Organic carbon reported from analysis of a source or ambient sample does not include the oxygens, hydrogens and other elements that comprise the organic carbonaceous matter.

Organic carbon matter is often called primary organic aerosol.

To approximate the amount of oxygen and hydrogen found in POA emissions use the formula:

- **POA = OC x 1.2**

Since particles in the atmosphere "age" through oxidation, a different "multiplier" is often applied to the POA to account for the further oxidation of the POA emissions:

- **POA = OC x 1.4 to 2.4**

1 - 18

Primary Organic Aerosols (cont.)

- Models only apply the additional multiplier to the POA, not the EC or SOA
- Multiplier is not related to the model's estimate of secondary organic aerosol formed in the atmosphere from precursor gases
- Only accounts for further oxidation of primary particle emissions as the aerosol "ages"
- Transport models contain a separate module to simulate the amount of secondary organic carbon formed in the atmosphere from precursor

1-18

Preparation of Fine Particulate Emissions Inventories

Atmospheric transport and transformation models contain the additional multiplier, but only apply it to the POA rather than the EC or SOA.

The multiplier is **not** related to the model's estimate of secondary organic aerosol formed in the atmosphere from precursor gases. It is only used to account for further oxidation of primary particle emissions as the aerosol ages.

Transport models contain a separate module to simulate the amount of secondary organic carbon formed in the atmosphere from precursor gases. The OCM of those particles is estimated directly by that module.

1 - 19

Primary Organic Aerosols (cont.)

- The derivation of a multiplier for ambient OC is much more complicated
- Use of a single multiplier introduces error
- A multiplier of 1.4 to 2.4 is often used for ambient data
- No agreed upon standard adjustment

1-19

Preparation of Fine Particulate Emissions Inventories

Deriving a multiplier for ambient OC is more complicated because the sample usually contains both POA and SOA, but the relative proportions of each are not known.

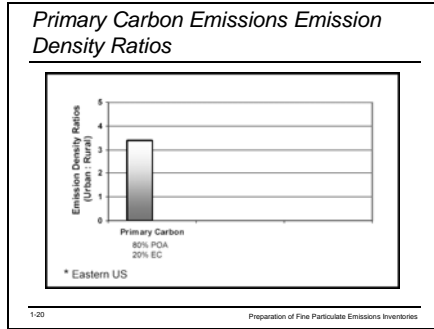
A single multiplier is applied to ambient OC, to adjust both primary and secondary OC in the sample.

Using a single multiplier introduces error, since multipliers probably would not be the same for both fractions.

A multiplier of 1.4 to 2.4 is often used for ambient data.

To date, there is no agreed upon standard adjustment that is consistently applied in either monitoring and modeling studies.

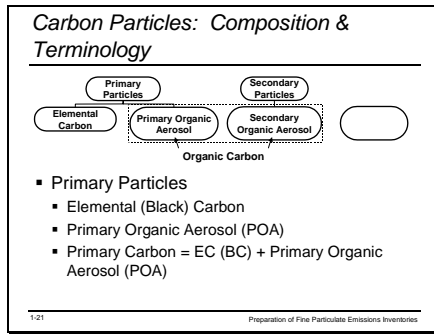
1 - 20



This graph compares emission density ratios for urban and rural carbon emissions.

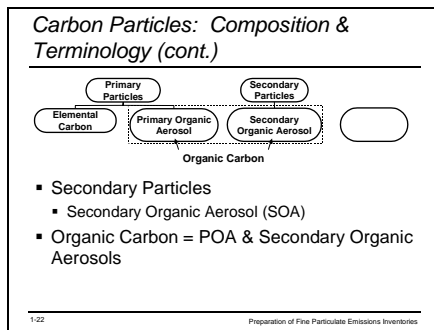
Primary carbon emissions are approximately three times higher in urban areas than in rural areas.

1 - 21



The primary particles comprise approximately 80% primary organic aerosols and 20% elemental carbon.

1 - 22

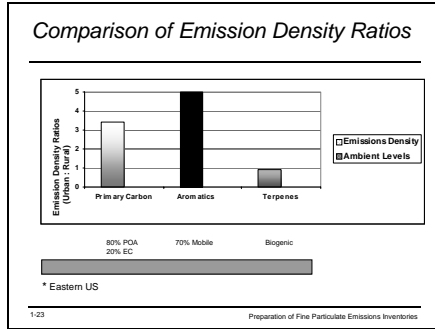


The condensable part of some EPA emission factors represents the vapor of organics when they are measured at stack temperatures.

The vapor condenses to form particles when the plume cools.

The condensable part of the emission factors is included in the POA emissions estimate.

1 - 23



Aromatics:

- VOC precursors that react to produce secondary organic aerosols
- Mobile sources produce 70 percent of aromatics (including benzene, toluene, and xylene)
- Toluene and xylene are the two aromatics that are generally associated with secondary aerosol formation
- The emission density of aromatics is about five times higher in urban areas than in the rural areas.
- The formation of SOA from these aromatic precursors is another potential cause of urban excess.

Terpenes:

- Major source of secondary organic aerosols
- Biogenic in origin as they are emitted by a variety of vegetation
- Emissions roughly equal when comparing a square mile of urban area to a square mile of rural area
- Trees in urban areas account for emissions there

1 - 24

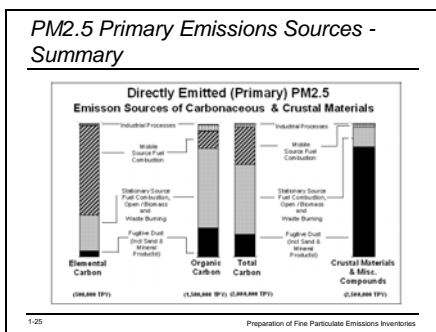
Summary of Important PM_{2.5} Source Categories

DIRECT EMISSIONS	PRECURSOR EMISSIONS	
Combustion <ul style="list-style-type: none"> Open Burning (all types) Non-Road & On-Road Mobile Residential Wood Burning Wastewater Power Gen Boilers (Oil, Gas, Coal) Boilers (Wood) 	SO₂ <ul style="list-style-type: none"> Power Gen (Coal) Boilers (Coal) Power Gen (Oil) Boilers (Oil) Industrial Processes 	NH₃ <ul style="list-style-type: none"> On-Road Mobile Animal Husbandry Fertilizer Application Wastewater Treatment Boilers
Crustal / Metals <ul style="list-style-type: none"> Fugitive Dust Mineral Prod Ind Ferrous Metals 	NO_x <ul style="list-style-type: none"> On-Road Mobile (Gas, Diesel) Power Gen (Coal) Non-Road Mobile (Diesel) Boilers (Gas, Coal) Residential (Gas, Oil) Industrial Processes 	VOC <ul style="list-style-type: none"> Biogenics Solvent use On-Road (Gas) Storage and Transport Residential Wood Petrochemical Industry Waste Disposal

1-24 Preparation of Fine Particulate Emissions Inventories

This chart summarizes the larger source categories of PM_{2.5} direct and precursor emissions.

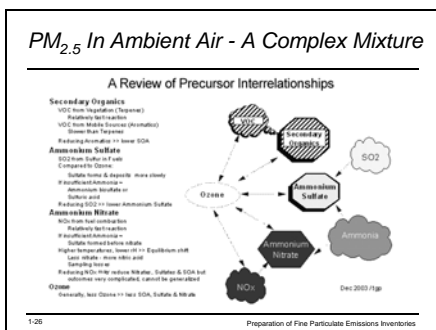
1 - 25



PM_{2.5} emissions:

- Combustion sources provide the majority of both elemental and organic carbon
- Most crustal materials are associated with fugitive dust
- Very little of the total carbon is associated with fugitive dust
- About 2 million tons of PM_{2.5} emissions per year, one-fourth of which is elemental carbon.
- Similarly, the emissions of crustal materials is about 2.5 million tons per year.
- Due to EI adjustments for carbon and crustal materials, (carbon emissions are increased while crustal emissions are reduced), carbon is usually found in much greater quantity on ambient PM_{2.5} samples.

1 - 26



Secondary organics:

- form from terpenes associated with VOC emissions (vegetation) occurs quickly
- form from aromatics associated with VOC emissions (mobile sources) occurs slower than the terpene reaction
- reducing aromatics can reduce SOA levels

Ammonium sulfate:

- forms from SO₂ emitted from the combustion of sulfur containing fuels
- forms and deposits slower than ozone
- can be transported much longer distances than either ozone or nitrate
- insufficient ammonia produces partially neutralized particles of ammonium bisulfate, or possibly sulfuric acid
- reducing emissions of SO₂ will lower ammonium sulfate concentrations

Ammonium nitrate:

- forms relatively quickly from NO_x emissions from fuel combustion

- insufficient ammonia reacts to form ammonium sulfate before forming ammonium nitrate
- higher temperatures and a lower relative humidity result in formation of less nitrate and more nitric acid
- reducing NO_x emissions may reduce nitrates, sulfates and secondary organic aerosols
- outcomes are complicated, involve ozone chemistry and can not be generalized

In conclusion, a reduction in VOC emissions would reduce ozone levels, resulting in less secondary organic aerosols, sulfate and nitrate formation.

The complex interactions among ozone formation, ozone precursors, sulfates, nitrates, and secondary organics must be collectively considered.

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